I. STUDIES IN THE CUSCOHYGRINE SERIES
II. THE STRUCTURE OF VINYL POLYMERS

BY

ROBERT CURTISS GUNTHER

A.B., Knox College, 1938

M.S., University of Illinois, 1939

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
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PART I

STUDIES IN THE CUSCOHYGRINE SERIES

INTRODUCTION

Hygrine and cuscohygrine are two of the alkaloids found associated with cocaine in certain varieties of coca leaves. Although the structure of hygrine has been definitely established as N-methyl-α-pyrrolidylacetone, investigations on cuscohygrine have not definitely proven its structure. Lieberman and Cybulski[1] have assigned to it the structure, *sym*-di(N-methyl-α-pyrrolidyl) acetone whereas Hess[2] believes it to possess an *unsym*-di(N-methyl-α-pyrrolidyl) acetone structure. The present work represents a study of certain reactions which would be valuable in the synthesis of Lieberman's symmetrical structure.

EXPERIMENTAL AND DISCUSSION OF RESULTS

N-Benzoyl-δ-aminobutyraldehyde has been synthesized from β-bromopropionaldehyde diethylacetal in good yields. Attempts to condense the substituted aminoaldehyde with acetone in accordance with a proposed phytochemical synthesis of hygrine and cuscohygrine by Robinson[3] were unsuccessful.

Prior to this work there have been two general methods available for the preparation of N-methyl-α-pyrrolidone, 1) that of Tafel and Stern[4] by the electrolytic reduction of N-methylsuccinimide, and 2) that of Späth and Lintner[5] involving the aminolysis of butyrolactone. A series of experiments indicated that the aminolysis method was the better of these two. A third method, however, involving the high pressure hydrogenation of N-methylsuccinimide according to the method of Wojcik and Adkins[6] proved to be superior to both the electrolytic and aminolysis methods from the point of view of adaptability and yield.

In an attempt to extend the Reformátsky reaction to compounds containing an amido-carbonyl group, viz. N,N-di-

methylbutyramide and N-methyl-α-pyrrolidone, it was found that the amido-carbonyl groups lacked the necessary degree of reactivity since in each case diethyl succinate, arising from the coupling of two moles of ethyl bromoacetate by zinc, was the only product isolated.

Ethyl ecgoninate, an oxidation product of ecgonine, was synthesized according to the following series of reaction: succinic anhyride → N-methylsuccinimide → N-methylpyrrolone-(2)-5-acetate → N-methylpyrrolidone(2)-5-acetate (ethyl ecgoninate).

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Part II.

THE STRUCTURE OF VINYL POLYMERS

Introduction

Despite the abundance of evidence cited for the proof of structure of most of the vinyl type polymers little conclusive data has been obtained for the structure proof of the polymers of acrylic acid and its derivatives. This research was undertaken to determine the structure of an alkyl acrylate polymer by comparing it with a commercially available acrylate polymer possessing a known 1,2-structure.

Experimental and Discussion of Results

The effects of different acid catalysts, namely hydrochloric acid and sulfuric acid, on the esterification of an ethylene-maleic anhydride copolymer possessing a 1.4:1 ratio of monomeric units, with methyl alcohol were studied. Results show that with hydrochloric acid as a catalyst esterification was

only 88 per cent complete whereas with sulfuric acid as a catalyst esterification was 99-100 per cent complete.

Methyl acrylate was polymerized by both the solution method using benzoyl peroxide as a catalyst and the emulsion method using hydrogen peroxide as a catalyst. The latter method proved very successful, the only difficulty encountered being in controlling the chain length. In all cases the polymers obtained possessed a molecular weight of between 30,000-40,000.

Ethyl succinate may be dehydrogenated by selenium dioxide to ethyl fumarate.[1] On this basis a methyl acrylate polymer would or would not undergo this type of oxidation depending upon whether it possessed a 1,2- or 1,3- structure. On the other hand the esterified ethylene-maleic anhydride copolymer should undergo this oxidation since it does possess a 1,2-structure. Preliminary experiments showed that the methyl acrylate polymer was not oxidized whereas the esterified copolymer was.

The polyamides and polyalcohols from both the esterified copolymer and the methyl acrylate polymer were prepared by the reaction of the methyl esters with ammonia[2] and phenyllithium[3,4] respectively. The work was discontinued at this point, however, since the writer accepted a position as research chemist on a National Defense Project.

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VITA

The writer was born in Galesburg, Illinois, April 17, 1916. He attended the public schools of that city and was graduated from Galesburg Senior High School in June, 1934. In the fall of 1934 he entered Knox College and received the degree of Bachelor of Arts in June, 1938. In September, 1938, he entered the Graduate School of the University of Illinois and received the degree of Master of Science in June, 1939. He held a University Scholarship during the academic year 1938-1939 and served as assistant in chemistry from September, 1939 to June, 1941. From September, 1941 to February, 1942, he held an Allied Chemical and Dye Fellowship and for the past four months he has been serving as a special research assistant in chemistry on a National Defense Project.

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